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(72) Inventors VERNON PETER SIMPSON and ALMA LONG COATS

(54) PROCESS FOR DYEING POLYMER SUBSTRATES

(71) We, HOOKER CHEMICALS & PLASTICS CORP., a Corporation organised and existing under the laws of the State of New York, United States of America, of Niagara Falls, State of New York, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a process for dyeing polymer substrates.

There is a continuing demand for low cost procedures for the coloration of molded plastics, especially reinforced polyester articles in such industries as the automotive, home appliance, radio and television industries and, for example, for use in decorative containers. The recent development of moldable reinforced polyester compositions characterized by little or no tendency to shrink during the curing thereof has brought with it the demand for suitable methods for the coloration of molded articles. Such polyester compositions are usually heterogeneous in nature, that is they are formulated to contain not only reinforcing materials, i.e. fiber glass and inorganic diluents such as talc and asbestos, but also two or more dissimilar organic polymer materials, e.g. mixtures of unsaturated polyesters with saturated polyesters, polymethyl methacrylate, polyvinyl chloride or polystyrene. On curing of the unsaturated polyester component as by cross linking with styrene or other ethylenic monomers, the dissimilar polymeric materials separate as a distinct phase giving rise to a distinctly heterogeneous polymer composition. Although on molding such polymer compositions, articles of superior surface smoothness and low shrinkage can be obtained, the heterogeneous nature of the composition creates problems in the coloration of such articles.

Thus, attempts to color the polymer composition by conventional pigmenting procedures result in uneven coloration of the molded article, due most likely to differences in the solubility or dispersibility of the pigment in the dissimilar polymers. Dyeing of these articles by conventional procedures also results in uneven colorations due to the dissimilar attraction of the polymers for the dyestuff, or the dyeing procedure may result in damage to the smooth surface of the molded article.

The present invention provides a process for dyeing a polymer substrate which comprises forming a coating on the substrate of a phosphorus sulfide in which the phosphorus has a valence of less than 5 and contacting the coated substrate with an aqueous liquor comprising an organic dyestuff and at least ont part by weight of a lignin sulphonate per part by weight of the organic dyestuff.

Dyestuff compositions suitable for use in the process of this invention are disclosed and claimed in USSN 376649.

In accordance with a preferred mode of carrying out the process of the present invention, a substrate consisting essentially of a polyester, and especially a polyester which has been cured by cross linking an ethylenically unsaturated polyester with an ethylenically unsaturated monomer, e.g. styrene, and containing a low profile additive, e.g. a saturated polyester containing terminal carboxyl groups, is contacted with an organic solvent solution of a phosphorus sulfide wherein the phosphorus has a valence of less than 5, e.g. phosphorus sesquisulfide, tetraphosphorus pentasulfide or tetraphosphorus heptasulfide, thereby forming on the surface of the substrate a phosphorus sulfide coating, and thereafter dyeing the coated substrate by contacting it with the aqueous liquor.

Typical polymers to which the process of this invention is applicable include the homopolymers and copolymers of ethylenically unsaturated aliphatic, alicyclic and aromatic hydrocarbons such as polyethylene, polypropylene, polybutene, ethylenepropylene copolymers, copolymers of ethylene or propylene with other olefins, polybutadiene; polymers,

of butadiene, polyisoprene, polystyrene and polymers of penene, hexene, cyclopentadiene, and methylstyrene. Other polymers useful in the invention include chlorinated polypropylene and chlorinated polyethylene; polymers of acrylate esters and polymers of methacrylate esters, acrylate and methacrylate resins such as ethyl acrylate; alkyd resins; cellulose derivatives such as cellulose acetate, cellulose acetate butyrate, cellulose nitrate or ethyl cellulose; epoxy resins; isobtylene resins (polyisobutylene); isocyanate resins (polyurethanes); melamine resins such as melamine-formaldehyde; phenolic resins such as phenol-formaldehyde; polyamide polymers, such as polyamides polyamide-epoxy and particularly long chain synthetic polymeric amides containing recurring carbonamide groups as an integral part of the main polymer chain; polyester resins such as unsaturated polyesters of dibasic acids and dihydroxy compounds, and polyester elastomer and resorcinol resins such as resorcinol-formaldehyde; rubbers such as natural rubber, synthetic polyisoprene, reclaimed rubber, chlorinated rubber, polybutadiene; polysulfides (Triokol); urea resins; vinyl resins such as polymers of vinyl acetal; polyvinylchloride, chlorinated polyvinylchloride; polyformaldehyde; polyphenylene oxide; polymers of diallyphthalates and phthalates; polycarbonates of phosgene or thiophosgene and dihydroxy compounds such as bisphenols, thermoplastic polymers of bisphenols and epichlorohydrin (tradename Phenoxy polymers); graft copolymers and polymers of unsaturated hydrocarbons and an unsaturated monomer, such as graft copolymers of polybutadiene, styrene and acrylonitrile, commonly called ABS resin; ABS - polyvinylchloride polymers, (tradename Cycovin); and acrylic polyvinyl chloride polymer, tradename Kydex 100).

Preferably, the polymer used as the substrate is a polyester in the cured state such as the cross linked polyester obtained from ethylenically unsaturated polyesters and an ethylenically unsaturated monomer, e.g. styrene, divinyl benzene, alpha methylstyrene and vinyl toluene. Especially preferred are the recently developed low profile polyester compositions comprising a mixture of a styrenated polyester resin and a dissimilar polymer, e.g. polymethylmethacrylate, polyvinyl chloride, polystyrene and saturated polyesters. Low profile polyester compositions of this class are disclosed in USP 3,701,748, USP 3,489,707, USP 3,711,432, USP 3,721,642 and British Patent Specification No. 1430874.

The polymer substrates can be used in the unfilled condition or with fillers such as glass fibers or mats, glass powder, asbestos, talc or other mineral fillers, wood flour or other vegetable fillers, or waxes.

The polymer substrates can be in various physical forms such as shaped articles, for example moldings, sheets and rods, fibers, films or fabrics of various thicknesses.

In the process of this invention the polymer substrate is first coated with one or a mixture of phosphorus sulfides, preferably phosphorus sesquisufide, in which the phosphorus has a valence of less than 5. In this step the phosphorus sulfide can be in the vapor or liquid state or dissolved in solvent. Preferably the phosphorus sulfide is dissolved in a solvent. Suitable solvents are those which do not detrimentally affect the surface of the polymer substrate but which may, and preferably do, have a swelling action on the surface of the substrate. Typical of such suitable solvents are halogenated hydrocarbons, and halocarbons such as, chloroform, methyl chloroform, phenyl chloroform, dichloroethylene, trichloroethylene, perchloroethylene, ethyl dibromide, ethyl chlorobromide, propylene dibromide, monochlorobenzene or monochlorotoluene; aromatic hydrocarbons such as benzene, toluene or xylene; ketones such as acetone or methylethyl ketone; acetic acid; acetic acid - trichloroethylene mixtures; and carbon disulfide. The solution concentration is generally in the range of 0.0001 weight percent of phosphorus sulfide, based on the weight of the solution, up to a saturated solution, preferably 0.1 to 2.5 weight percent. Generally, the temperature of this first treatment step is in the range of 10 to 135°C, but is preferably 25 to 50°C. The contact time varies depending upon the nature of the substrate, concentration of the phosphorus sulfide solution, temperature and depth of coloration desired, but is generally in the range of 1 second to 1 hour or more, preferably 1 to 10 minutes.

Prior to contacting the polymer substrate with the phosphorus sulfide, liquid or solution, the surface of the substrate should be clean. When a solution is used, the solvent generally serves to clean the surface. Preferably, a solvent wash to remove dirt or grime such as grease, wax or mold release agents, is employed prior to contacting the substrate with the phosphorus sulfide liquid or solution, to improve the adhesion and quality of the resulting coating and subsequent dyeing. The temperature of the solvent wash is generally in the range of 30°C to the boiling point of the solvent used, preferably 50 to 100°C or higher. The contact time varies according to the condition of the substrate but preferably is from 1 to 15 minutes.

As a result of the treatment with the phosphorus sulfide compound, the latter is deposited at the surface of the polymer substrate. By this is meant that it can be located at the surface of the substrate, embedded in the surface and embedded beneath the surface of the substrate. The resultant surface is thereby rendered more receptive to organic

dyestuffs, parti[illegible]ly of the basic dyestuff class than the untreated substrate.

Following this initial treatment or pretreatment, of the substrate, it may be rinsed with a solvent and can then be dried by merely exposing the substrate to the atmosphere or to inert atmospheres such as nitrogen or carbon dioxide, or by drying the surface with radiant heaters or in a conventional oven. Drying times can vary considerably, for example, from 1 second to 30 minutes or more, preferably from 5 seconds to 10 minutes and more preferably 5 to 120 seconds. The rinsing and drying steps are optional.

The treated polymer substrate is thereafter contacted with the aqueous liquor. Preferably, in carrying out this dyeing step of the process of this invention, an aqueous dye bath is prepared containing 1 to 40 parts by weight of the dyestuff composition per 100 parts by weight of water, preferably 5 to 30 parts by weight of dyestuff composition per 100 parts by weight of water. The resulting dye solution is rendered alkaline to a pH of 9 to 12 by the addition of an alkaline agent, e.g. sodium hydroxide or sodium carbonate. The bath is then heated to 30 to 100°C preferably 50 to 80°C and the pretreated polymer substrate entered into the bath. The substrate is maintained in contact with the dye liquor or bath for 5 to 60 minutes or more, preferably 20 to 40 minutes. Thereafter the dyed substrate is removed from the dye bath, washed with warm (40 to 60°C) water and dried in air or in a warm (40 to 80°C) oven. The dried dyed polymer substrate can, if desired, be scoured by boiling in water or dilute soap solution for 5 to 10 minutes.

The depth of shade of the coloration produced may be varied either by controlling the dyestuff concentration of the dye bath or by controlling the time of contact of the pretreated polymer substrate with the dye bath. Thus, light or pastel shades can be obtained by carrying out the dyeing in a dilute dye bath, e.g. a dye bath containing one or two parts by weight or less of dyestuff composition per 100 parts by weight of water or by exposing the polymer substrate in more concentrated dye baths for relatively short times e.g., about 5 or slightly more minutes.

Depending upon the size and physical form of the polymer substrate, other means of contacting the substrate with the dye liquor can be used. Thus, relatively large molded objects may be dyed by placing the object in a suitable container and circulating the dye liquor around and over the stationary object. Films, fibers and fabrics can be dyed by the conventional pad liquor, dipping or spraying techniques known and practiced in the dyeing art.

The colorations produced by the process of this invention are fast to rubbing, organic solvents, alkalis, and light. The colorations produced are level, i.e. they are substantially free from the marble-like effects obtained by the conventional pigmentation processes and when the substrate are dyed directly (i.e. without pretreatment according to this invention with phosphorus sulfides) with organic dyestuffs. Although the colorations are essentially confined to the surface of the polymer substrate, they are permanently bonded to the surface and conceal it sufficiently to give pleasing and uniform aesthetic effects even over such heterogeneous materials as "low profile" styrenated polyesters containing dissimilar polymers, glass fibers, voids and inorganic fillers.

The following Examples will illustrate the invention. In these Examples, all part and percentages are by weight and temperatures are given in degrees centigrade, unless otherwise specified.

EXAMPLE I

A molded plaque, measuring 8 in. × 8 in. × 1/8 in., from the "low profile" reinforced polyester composition prepared as described in Specification No. 11430874 was solvent washed by immersion in a hot (70°) perchloroethylene bath for two minutes. The washed plaque was removed from the bath and dried in air for 1 minute. The plaque was then immersed in a warm (35° to 40°) solution of one percent phosphorus sesquisulfide in perchloroethylene for five minutes. The pretreated plaque was then dried in air for one minute following which it was immersed in aqueous dye bath containing 20 parts of a dyestuff composition containing 20 parts of sodium lignin sulfonate and one part of Brilliant Cresyl Blue, Colour Index Number 51010, and 80 parts of water, to which sufficient aqueous caustic soda had been added to adjust the pH of the bath to about 11.0. The bath was heated to and maintained at about 75° for thirty minutes. During this period the bath was agitated intermittently. The dyed plaque was removed from the bath and rinsed in warm water and then dried in a circulating air oven at 75° for 20 minutes. The dyed plaque was colored a deep level shade of green and was free from mottled effects. On boiling in water for 5 minutes there was substantially no bleeding of dye into the water.

EXAMPLE II

A portion, measuring 3 in. by 2 in. of polypropylene split film was solvent washed by immersion in warm (50°) perchloroethylene for two minutes. The washed film was removed from the bath and dried in air for one minute. The film was then immersed in a warm (35°) solution of 1% phosphorus sesquisulfide in perchloroethylene for five minutes. The pretreated film was dried in air for six minutes and then immersed in an

aqueous dye bath containing 20 parts of sodium lignin sulfonate, 5 parts of Sevron Orange, 500 parts of water and sufficient caustic soad to adjust the pH of the bath to about 10.0. The film was held in the dyebath at 35° to 40° for thirty minutes, stirring the bath intermittently. Thereafter the dyed film was rinsed in hot water and dried in a 75° oven for 10 to 15 minutes. The deep orange colored polypropylene film was fast to boiling water, i.e., the dyed film could be held in boiling water for five minutes without noticeable bleed of the dye into the hot water bath.

By repeating the above dyeing procedure but omitting the pretreatment with phosphorus sesquisulfide, only a very slight staining of the polypropylene film occurred.

EXAMPLE III

In a similar manner to that in Example II, a 3 in. × 2 in. portion of polyvinyl chloride film was solvent rinsed in perchloroethylene for two minutes dried in air for one minute and then pretreated by immersion in a warm (35°) 1% phosphorus sesquisulfide-perchloroethylene solution for five minutes. The film was dried in air for six minutes and dyed in an alkaline (pH 10.0) aqueous dyebath containing 20 parts of sodium lignin sulfonate and one part of Victoria Blue B dissolved in 500 parts of water. The dyeing was accomplished in 30 minutes at 65°. The film was dyed a medium blue shade which was fast to boiling water.

EXAMPLE IV

A molded polybutene plaque, measuring 3 in. × 2 in. × 1/8 in., was pretreated by immersion in a warm (45°) 1% phosphorus sesquisulfide-perchloroethylene solution for five minutes. The plaque was dried in air for six minutes and then dyed by immersion in an alkaline (pH 10.0) aqueous dyebath containing 20 parts of sodium lignin sulfonate and one part of Auramine O dissolved in 500 parts of water. The dyeing was effected at 70° for 30 minutes. The dyed plaque was rinsed in warm water and dried in a 75° oven for five minutes. The polybutene plaque was dyed a pastel yellow shade which was fast to hot water.

EXAMPLE V

A portion of solid amber colored polyurethane sheet, measuring 3 in. × 3 in. × 1/4 in., was solvent washed in hot (65°) perchloroethylene for two minutes. The washed sheet was air dried for one minute and then pretreated by immersion in a warm (35°) 1% phosphorus sesquisulfide - perchloroethylene solution for five minutes. The pretreated polyurethane was dried in air for six minutes and then dyed by immersion in an alkaline (pH 10.0) aqueous dyebath containing 20 parts of sodium lignin sulfonate and one part of Brom Cresyl Blue dissolved in 500 parts of water. The dyeing was carried out at 75° for 30 minutes. The dyed sheet was rinsed with warm water and dried in a 75° oven for ten minutes. The deep bluish black dyed polyurethane was fast to hot water.

EXAMPLE VI

A square molded plaque of high density polyethylene, weighing about 25 parts was solvent washed by immersion in hot (85°) perchloroethylene for about five minutes. After drying in air for about one minute, the washed plaque was pretreated by dipping in a warm (40°) 1% solution of phosphorus sesquisulfide in perchloroethylene for five minutes. The pretreated plaque was dyed a bright orange shade by immersing it in an alkaline (pH 10.0) aqueous dyebath containing about 20 parts of sodium lignin sulfonate and one part of Acridine Orange dissolved in 500 parts of water at 80° for 30 minutes. The dyed plaque was rinsed with hot water and dried in a 75° oven for 30 minutes. The dyed plaque was fast to boiling water.

EXAMPLE VII

A blow molded low density polyethylene bottle was solvent washed by immersion in hot (70°) perchloroethylene for two minutes and thereafter it was dried in air for about one minute. The bottle was pretreated by immersion in a warm (35°) 1% solution of phosphorus sesquisulfide in perchloroethylene for five minutes. The pretreated bottle was dyed a pale organge shade by immersion in an alkaline (pH 10.0) aqueous dyebath containing 20 parts of sodium lignin sulfonate and one part of Acridine Orange dissolved in 500 parts of water. The dyed bottle was rinsed in hot water and dried in 75° oven for 10 minutes. The dyed bottle was fast to hot water.

EXAMPLE VIII

A molded household mixer housing formed from ABS polymer (Marbon GSM) and weighing about 75 parts was solvent washed by immersion in hot (70°) perchloroethylene for about two minutes. The washed housing was air dried for about one minute and then pretreated by immersion for five minutes in a warm (35°) 1% solution of phosphorus sesquisulfide in perchloroethylene. After being dried in air for about six minutes, the housing was dyed by immersion for 30 minutes in a hot (75°) alkaline (pH 10.0) aqueous dyebath containing 20 parts of sodium lignin sulfonate and one part of Brilliant Cresyl Blue in 500 parts of water. The deep blue colored housing was rinsed with hot water and then dried in a 75° oven for 10 minutes. The dyed housing was fast to boiling water.

WHAT WE CLAIM IS:—

1. A process for dyeing a polymer substrate which comprises forming a coating on the substrate of a phosphorus sulfide in which the phosphorus has a valence of less than 5 and contacting the coated substrate with an aqueous liquor comprising an organic dyestuff and at least one part by weight of a lignin sulphonate per part by weight of the organic dyestuff.

2. A process according to claim 1 wherein the phosphorus sulfide is phosphorus sesquisulfide.

3. A process according to claim 1 or 2 wherein the coating is formed by treating the substrate with a solution of the phosphorus sulfide in an organic solvent.

4. A process according to claim 3 wherein the solution contains from 0.1 to 2.5 weight percent of phosphorus sesquisulfide.

5. A process according to claim 3 or 4 wherein the organic solvent is perchloroethylene.

6. A process according to any one of the preceding claims wherein the substrate is of a polyester.

7. A process according to claim 6 wherein the polyester is a crosslinked polyester obtained from an ethylenically unsaturated polyester and an ethylenically unsaturated monomer.

8. A process according to claim 7 wherein the crosslinked polyester has been obtained from an ethylenically unsaturated polyester and styrene.

9. A process according to claim 7 or 8 wherein the substrate also comprises a dissimilar polymer selected from polymethylmethacrylate, polyvinyl chloride, polystyrene and a saturated polyester.

10. A process according to claim 9 wherein the dissimilar polymer is a carboxyl group terminated saturated polyester.

11. A process according to any one of claims 6 to 10 wherein the polyester contains a filler.

12. A process according to any one of claims 1 to 5 wherein the substrate is of polypropylene.

13. A process according to any one of claims 1 to 5 wherein the substrate is of polyethylene.

14. A process according to any one of claims 1 to 5 wherein the substrate is of a graft copolymer of polybutadiene, styrene and acrylonitrile.

15. A process according to any one of claims 1 to 5 wherein the substrate is of polyvinylchloride.

16. A process according to any one of the preceding claims wherein the substrate is washed with a solvent before the coating of the phosphorus sulfide is formed thereon.

17. A process according to any one of the preceding claims wherein the aqueous liquor contains about 20 parts by weight of a lignin sulfonate per part by weight of organic dyestuff.

18. A process according to any one of the preceding claims wherein the lignin sulfonate is a sodium lignin sulfonate.

19. A process according to any one of the preceding claims wherein the aqueous liquor is an alkaline aqueous dyebath.

20. A process according to Claim 19 wherein the dyebath has a pH of from 9 to 12.

21. A process according to Claim 1 substantially as described in any one of the Examples.

22. Polymer substrates when dyed by a process as claimed in any one of the preceding claims.

J. A. KEMP & CO.,
Chartered Patent Agents,
London WC1R 5EU.
14 South Square, Gray's Inn,

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